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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Emanuel I. Cooper, et al.

Examiner: John P. Sheehan

Serial No: 09/634,171

Art Unit: 1742

Filed: August 9, 2000

Docket:ARC920000067US1(13521)

For: CoFe ALLOY FILM

Date: February 13, 2004

Commissioner for Patents
P.O. Box 13450
Alexandria, VA 22313-1450

DECLARATION OF HONG XU UNDER 37 C.F.R. § 1.132

Sir:

I, Hong Xu, hereby declare and say that:

(1) I am one of the applicants named in U.S. Application Serial No.

09/634,171, filed with the United States Patent and Trademark Office on August 9, 2000;

(2) I am familiar with the subject matter disclosed in U.S. Application

Serial No. 09/634,171, filed August 9, 2000; and have reviewed the applied reference,

namely the article to E.M. Kakuno, et al., entitled "Structure, Composition, and

Morphology of Electrodeposited $\text{Co}_x\text{Fe}_{1-x}$ Alloys", J. Electrochemical Soc., Vol. 144, No.

9, September 9, 1997 pp. 3222-3226 (hereinafter "Kakuno, et al.") that was cited in the

Office Action dated September 15, 2003;

(3) Additional experiments and data have been carried out to establish that

the claimed composition is not obvious relative to the disclosure of Kakuno, et al. cited

by the Examiner in the Office Action dated September 15, 2003. Specifically,

experiments were performed to show differences between the inventive CoFe film and a

film that was reproduced in accordance with the disclosure of Kakuno, et al. We also

measured the film composition, magnetic moment, resistivity, B-H loops, crystallinity and impurity concentration of the film prepared in accordance with the Kakuno, et al., disclosure and compared them to the CoFe film of the present invention. We also measured oxygen and nitrogen concentration in the plated films;

(4) The experiments performed and reported in this Declaration were conducted by me, or they were carried out under my direct supervision or control;

(5) Specifically, experiments have been performed to show that the cobalt-iron binary alloy electroplated film of the present invention has different properties as compared with the films that are obtained using the procedure disclosed in the Kakuno, et al. disclosure. Specifically, in the present invention a CoFe alloy composition prepared in accordance with the present invention was compared to the same alloy composition that was prepared in accordance with the disclosure of Kakuno, et al.

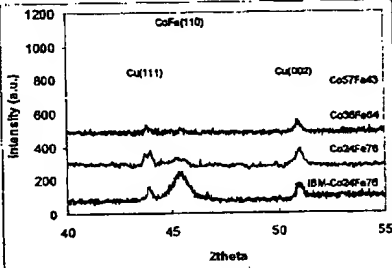
The properties of the electroplated CoFe films plated using the process of the present invention, as demonstrated herein, are significantly different from the CoFe films obtained using the process disclosed in Kakuno, et al. Since the present application and Kakuno, et al. use different plating processes, experimental data comparing the two different techniques were conducted and the data provided herein shows that the alloy properties of electroplated CoFe films are not only related to alloy composition, but are also determined by other processing factors including the electroplating conditions, such as bath chemistry, with or without additives, mixing, current density, pH, temperature and magnetic field.

The data provided herein also shows that CoFe films produced using the Kakuno, et al. procedure have a high impurity concentration of oxygen (5.7 atomic %)

and nitrogen (0.19 atomic %) as compared to the claimed films of the present application which are recited to be substantially free of oxygen. This provides further support that the plating conditions affect alloy properties.

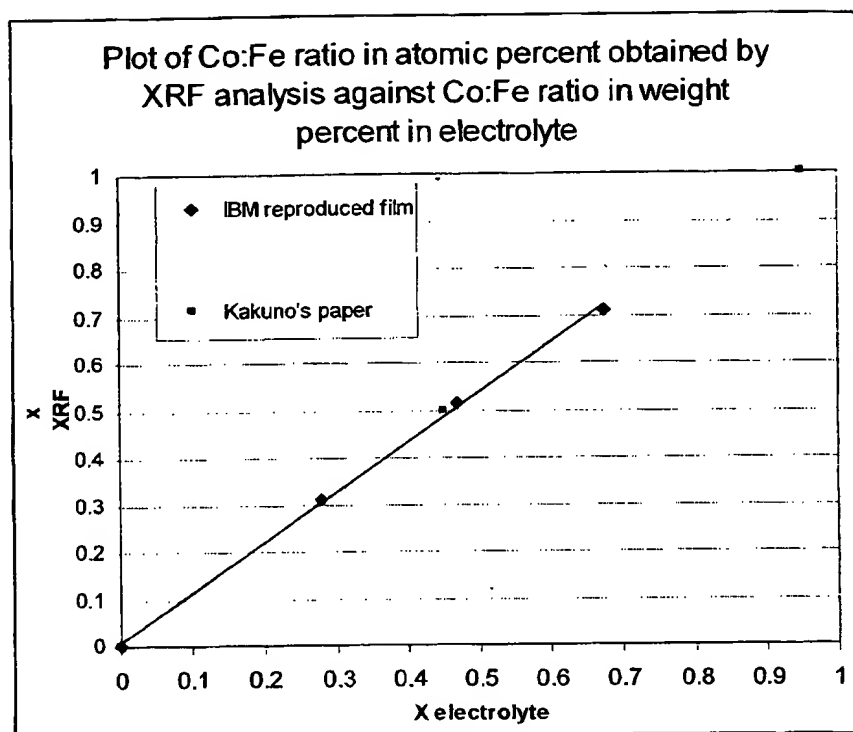
Magnetic properties, especially magnetic moment, are extremely sensitive to impurity concentrations in the films. All the applicants of the present application have experience with an additive free bath. One of the spirits of the present application was to invent an innovative way to prevent CoFe from oxidation during plating, and to use a sulfate only bath to prevent the other impurity incorporation such as nitrogen, thus high magnetic moment of at least 2.3 Tesla can be achieved. It is noted that the present application doesn't preclude the presence of some oxygen and iron oxide in the plated CoFe film. However, in order to achieve the magnetic moment of at least 2.3 Tesla, the plated CoFe films have to be substantially free of oxygen and other impurities such as nitrogen. By comparing the magnetic moment and resistivity of the inventive films and the Kakuno's films provided herein, we have shown that in order to achieve a high magnetic moment of at least 2.3 Tesla, the plated CoFe films have to be substantially free of oxygen and other impurities.

(6) The purpose of the following experiments aim to reproduce the CoFe films produced using the process disclosed in Kakuno, et al. using the conditions disclosed therein and to compare the prior art films to the films of the present invention. The follow table provides a description of the experimental set up that was used by us to form CoFe films provided in the Kakuno, et al. disclosure. The experimental procedure is similar to the one employed in Kakuno, et al. We also provide an explanation for any deviations from the procedure described in Kakuno, et al.

	Kakuno's paper	Reproduced conditions used	Explain the differences
Plating system	Stationary parallel plate; Pt counter electrode; Ag/AgCl reference electrode	Stationary parallel plate; 250 ml solution in beaker Pt counter electrode; Hg/HgSO ₄ reference electrode	In Kakuno, et al., there is no information for the volume of the solution. A 250 ml solution was chosen for convenience. A different reference electrode was used. All potentials are versus Hg/Hg ₂ SO ₄ reference, which is 0.4 V more positive than Ag/AgCl as reported in the paper. So the -1.6 V corresponds to Kakuno, et al. -1.2 V.
Power supply	EG&G PAR potentiostat/galvanostat (Model 273A)	EG & G PAR potentiostat/galvanostat (Model 273A)	
Substrate	(100) textured polycrystalline Cu plates mechanically polished with 1um diamond and then chemically polished. Area of plates: 0.80 cm ² (see Figure 4 in Kakuno's paper for the structure of the substrate)	(100) textured polycrystalline Cu disks mechanically polished with 1um diamond Area of plates: 0.98 cm ² The following graph is the x-ray diffraction data for the Cu substrate and reproduced CoFe films 	When one compares the X-ray diffraction data between Kakuno, et al. and XRD data of the present invention, one will find that the Cu disks have the same structure as Kakuno's plates, indicated by the same 2 theta location for the Cu (111) and Cu (002). The intensity of the peak is proportional to metal thickness. The striking difference, as shown by the magnitude of the Co(110) peak, is in the much lower degree of apparent crystallinity in the high-Fe Kakuno compositions (Fe64 and Fe76) as compared to the Fe76 film of the present invention. This means that the grains in the Kakuno films are much smaller and that the relative volume of intergranular space (proportional to intergranular area) is much larger, and/or that the Kakuno films are much less textured, again probably due to intergranular phases interfering with textured crystal growth.
Bath chemistry	Reagent grade Cobalt Sulfate and Iron Ammoniac Sulfate immediately prior to each experiment; X molar of metallic cobalt and 1-x molar of metallic iron.	Reagent grade Cobalt Sulfate and Iron Ammoniac Sulfate immediately prior to each experiment; X molar of metallic cobalt and 0.7-x molar of metallic iron.	We can't dissolve required Cobalt Sulfate and Iron Ammoniac-Sulfate for 1M concentration at room temperature of 21 °C in our lab even overnight. In order to have a freshly prepared bath, 0.7M solution was used for plating. 0.7M concentration is

			already a highly concentrated solution. Study found that plated film composition is related to the ratio of $\text{Fe}^{2+}/\text{Co}^{2+}$ in the solution, not the absolute solution concentration (See results and discussion section).
Temperature	Room temperature; exact value not reported	Room temperature of 21 °C	None
Magnetic field	not mentioned	Not applied	None
PH	As prepared, not adjusted; not reported	As prepared, not adjusted; measured pH=3.55	None
Potential (V)	-1.0, -1.2, -1.4	-1.2	Since a different reference electrode was used, the potential for the condition shown is after conversion.
Surface quality	Shiny surface	Dark shiny surface	Kakuno, et al. didn't mention whether the film is dark shiny or bright shiny.

(7) Three CoFe samples (with Fe wt% 31.5, 51.7, 71.1, <1micron) were plated in the stationary system using Kakuno, et al. plating conditions described above. Our study shows that plated CoFe film composition is related to the iron/cobalt ratio in the solution, not the absolute concentration of Fe or Co in the solution. This result agrees with Kakuno, et al. as shown in the following graph.



The figure shown above is provided to explain our rational for using the bath chemistry mentioned in the above table. We attempted to use the same concentration of 1M cobalt sulfate and iron ammoniac-sulfate as described in the Kakuno, et al. paper. However, we couldn't dissolve 1M cobalt sulfate and iron ammoniac-sulfate as used in the Kakuno, et al. article at room temperature in our lab even overnight. In order to have a freshly prepared bath, a 0.7M solution was used for plating. A 0.7M solution is a highly concentrated solution. The above figure shows that plated film composition is related to the ratio of $\text{Fe}^{2+}/\text{Co}^{2+}$ in the solution, not the absolute concentration. This figure agrees with Kakuno, et al. Hence, the figure shows that although we didn't use the same absolute salt concentration for the experiments as described in the Kakuno, et al. paper, absolute salt concentration won't effect the film concentration.

Since Kakuno's CoFe films were plated in a system without magnetic field, the films show isotropic properties instead of anisotropic properties of the inventive CoFe films. Because of this isotropic behavior, magnetic moment data can't be obtained. (Loops are attached in Exhibit 1; the three loops are for the prior art film, while the fourth is for the film of the present invention.)

In order to obtain magnetic moment values for Kakuno's CoFe films, two 5" wafers were plated with CoFe films using Kakuno's chemistry in a paddle cell plating system as indicated in the present application. This system has 800 Oe magnetic field applied perpendicular to the paddle moving direction. Kakuno's plating chemistry, room temperature, pH not adjusted (measured pH=3.55) and current density of 20 mA/cm² were used. CoFe films using Kakuno's plating chemistry show anisotropic behavior, which enables us to measure the magnetic properties. The composition for both films is Fe65wt.%. Study shows that Kakuno's films are dark and shiny and are very brittle. After low temperature annealing at 250°C for 8hrs, the film broke completely into small pieces. In contrast, the inventive CoFe films, at this composition, are still intact after annealing. Fig 5 in Kakuno's paper shows cracks in the plated films, confirming this finding. Exhibit 2 is an original photocopy of page 3225 of the Kakuno, et al. paper that clearly shows the presence of cracks. This is especially seen in Fig. 5b. An attached optical photograph of the reproduced Kakuno's film also shows cracks. See Exhibit 3. Exhibit 3 also shows an optical photograph of the inventive sample itself which doesn't show any cracks therein. The magnetic moment for Kakuno's films is 2.2 Tesla compared with 2.4 Tesla for the inventive films at this composition. The resistivity of Kakuno's films at Fe 65wt.% is 44μΩ-cm, while the inventive films at this composition

is $38\mu\Omega\text{-cm}$. The low moment and high resistivity of Kakuno's CoFe films indicate high levels of impurity concentration in the plated films, which was confirmed by the impurity data discussed in the following pages. We also studied the crystallinity for both inventive and Kakuno's films as shown in Exhibit 4. X-ray diffraction was used to study the crystallinity of the plated films. By comparing the figure in Exhibit 4 and Figure 4 in Kakuno's paper, one will find that the Cu disks we used as substrates for plating had the same structure as Kakuno's plates, indicated by the same 2θ location for the Cu (111) and Cu (002). The intensity of the peak is proportional to Cu plate thickness. The striking difference, as shown by the magnitude of the Co(110) peak, is in the much lower degree of apparent crystallinity in the high-Fe Kakuno compositions (Fe64 and Fe76) as compared to the Fe76 film of the present invention, where the degree of crystallinity of the plated film is related to the number of peaks and the intensity of these peaks. This means that the grains in the Kakuno films are much smaller and that the relative volume of intergranular space (proportional to intergranular area) is much larger, and/or that the Kakuno films are much less textured, again probably due to intergranular phases interfering with textured crystal growth. Since the inventive film and Kakuno's film were plated on the same Cu substrates, the difference in grain structure came from the plated film itself. The finer crystalline grain size and/or the lesser degree of texturing of Kakuno's films as shown by X-ray diffraction, at least for Fe 64wt% and 76wt%, is completely consistent with a higher level of impurities, because of a relatively larger intergranular area occupied by a larger relative volume of impurities that interfere with orderly crystal growth.

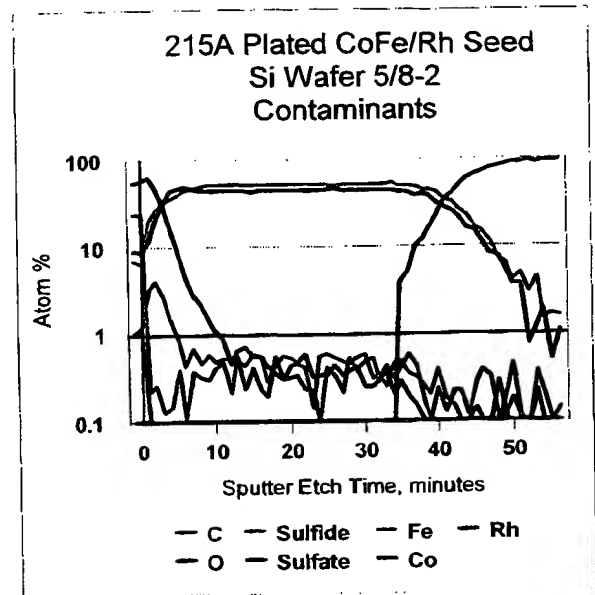
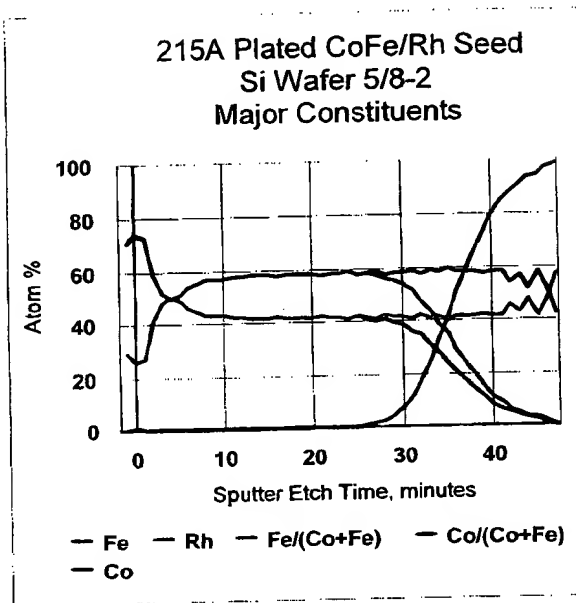
Phi Quantum 2000 Electron Spectroscopy for Chemical Analysis (ESCA)

was used to analyze the impurity concentration in the plated CoFe films due to its high accuracy in low-level impurity analysis. 5" CoFe films were plating in a paddle cell using Kakuno and the inventive bath chemistry and plating conditions, respectively. The plated film composition is around Fe60 and Co40 for both films. ESCA depth profiles show that Kakuno's film has oxygen content in the bulk as high as 5.7 atomic %, while the bulk oxygen content in the inventive film is well below 1 atomic %. ESCA data also shows that Kakuno's film has nitrogen content of 0.19 atomic %, while the inventive film is nitrogen free. This is because Kakuno's bath contains Iron Ammoniac Sulfate, while the bath of the present invention has no N-containing constituents.

The reason why impurities such as O or N can reduce the magnetic moment is that the bulk magnetic moment is a function of the density of atomic magnetic moments per unit volume. The presence of O and N impurities dilutes the magnetic moment by reducing the volume fraction of the magnetic atoms Fe and Co. Furthermore, oxygen converts a portion of the high-moment Fe and/or Co into low or zero moment oxide compounds such as Fe_2O_3 , Fe_3O_4 , CoFe_2O_4 , FeO or CoO which all have much lower magnetic moment than Fe and Co.

The ESCA analysis for the inventive film and for the Kakuno, et al. film are now shown:

ESCA profile for the inventive film:

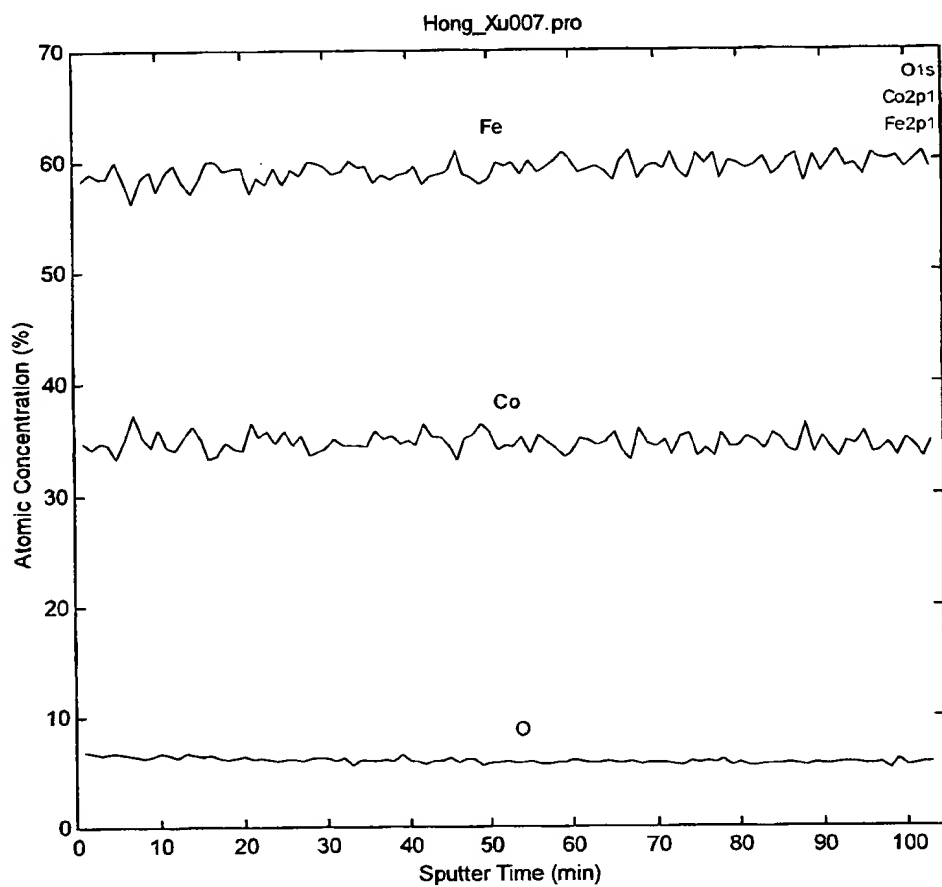


During the analysis, the film was sputtered away and the Co, Fe and oxygen concentration were analyzed (The same was performed on the inventive film). Here, sputter time corresponds to the film thickness. At zero sputter time, the concentrations shown are at the film surface. The above figures show the concentration profile throughout the film. Most importantly, the oxygen concentration for the inventive film was less than 1 atomic % in the bulk.

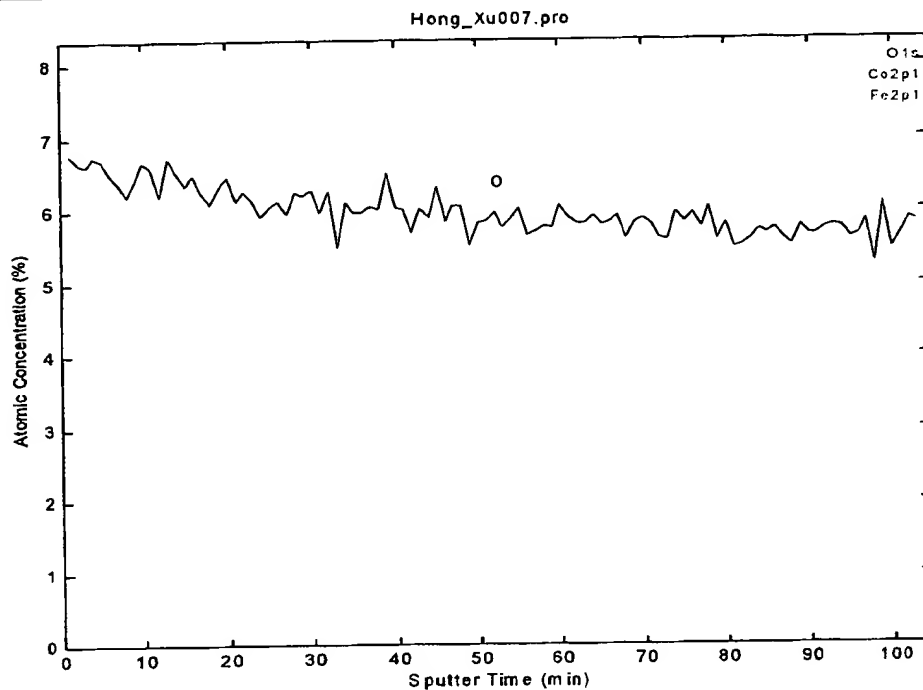
The following Figure is ESCA profile for Kakuno's film. The profile shows that the oxygen concentration for Kakuno's film was as high as 5.7 atomic% in the bulk.

ESCA profile for Kakuno's film

Hong_Xu007.pro: Sulfate + Ammonium CoFe Plated Wafer: Sulfate + Ammonium CoFe Plated Waf Hitachi GST/SJ
6.7807e+000 max
Fe2p1/Area1: MD perp exit



Hong_Xu007.pro: Sulfate + Ammonium CoFe Plated Wafer: Sulfate + Ammonium CoFe Plated Waf Hitachi GST/SJ
6.0971e+001 max
Fe2p1/Area1 MD perp exit



Specie	O	N	Sulfide	Sulfate	Co	Fe
Atom %	5.7	0.19	0.062	0.019	35	59

The above figure is a closer look at the oxygen concentration shown in the figure on the previous page of this declaration. Specifically, this figure shows that the oxygen concentration for the prior art film disclosed in Kakuno, et al. is very high, not only on the film surface, but in the bulk as well. The above table shows that the average

bulk concentration of oxygen for Kakuno's film was as high as 5.7 atomic%, and nitrogen was 0.19 atomic %.

(8) Summary: The experiments in this declaration were performed to show differences between the inventive CoFe film and a film that was reproduced in accordance with the disclosure of Kakuno, et al. The table, which is provided above, illustrates that the same plating set-up as disclosed in the prior art paper was used as well as the same substrates for plating. We measured the film composition, magnetic moment, resistivity, B-H loops, crystallinity and impurity concentration of the film prepared in accordance with the Kakuno and compared them to the CoFe film of the present invention. We also measured oxygen and nitrogen concentration in the plated films.

These study shows that there are major differences between Kakuno's CoFe films and the inventive films at the same composition. Kakuno's film has lower magnetic moment of 2.2 Tesla and higher resistance compared with the inventive films ~~at the same composition~~. Kakuno's films show much less crystallinity in X-ray diffraction, i.e., have finer grain size and/or less texturing. Kakuno's films are very brittle and collapsed after annealing at a relatively low temperature. All these indicate that Kakuno's films have high levels of impurities incorporated to the plated films. ESCA data confirmed that Kakuno's film has high oxygen content, as high as 5.7 atomic%, and substantial nitrogen content, 0.19 atomic %, while the inventive film has bulk oxygen concentration well below 1 atomic % and is nitrogen-free.

Kakuno's electroplating process is a different process from the inventive CoFe plating process. We proved that CoFe film properties are determined not only by composition, but also by micro-structure of the film and impurity concentration, which

are directly affected by electroplating conditions. Kakuno used Iron Ammoniac Sulfate bath without any additives, while in the present invention a purely sulfate bath with an additive to prevent the impurity incorporation into the plated films is used. Study shows that although current density in Kakuno's paper is $10-50\text{mA/cm}^2$, which overlaps the disclosed $3-40\text{mA/cm}^2$, plating bath chemistry is the key to plate a high moment CoFe films with extremely low oxygen and free of nitrogen impurities, which directly affect the plated film properties.

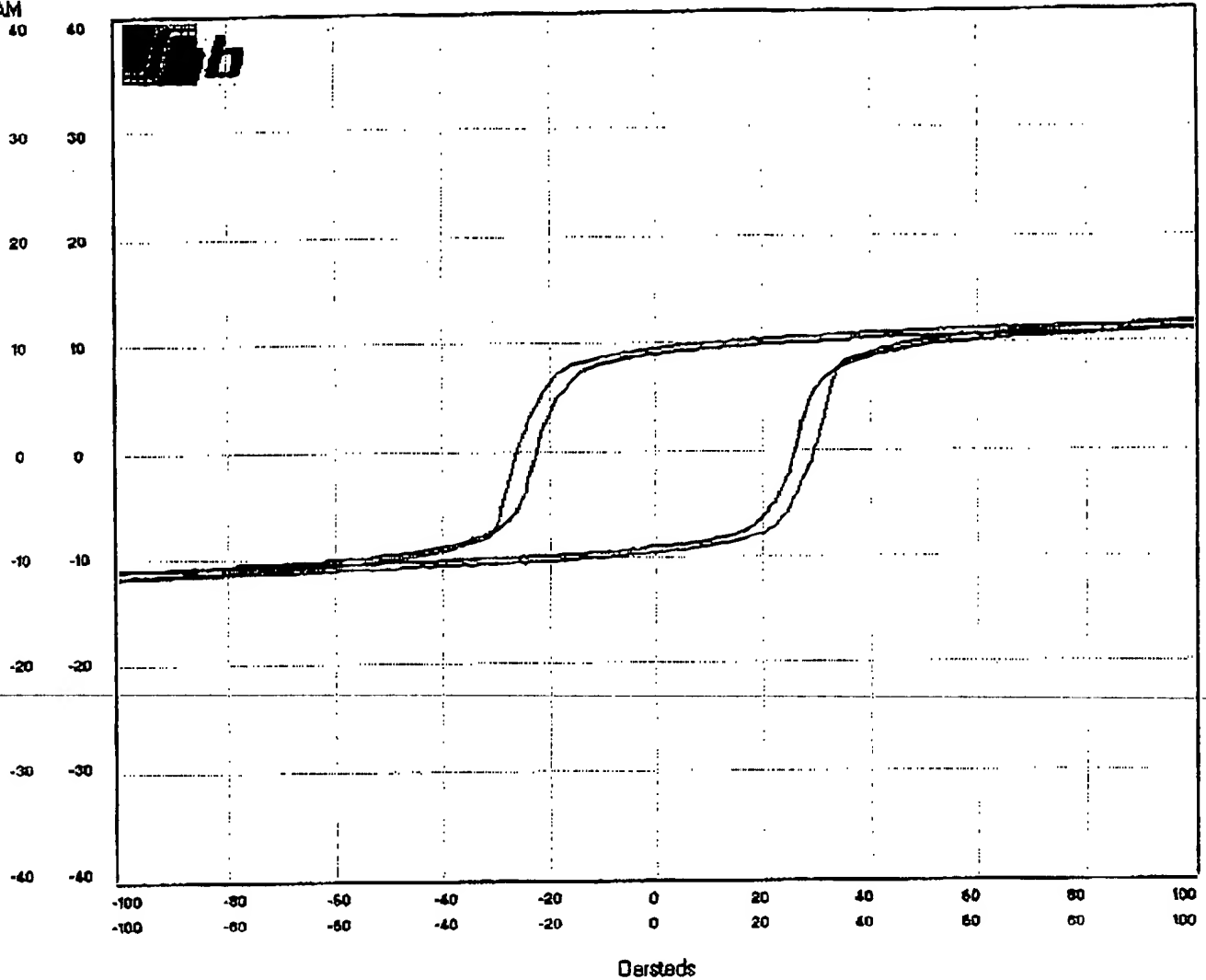
(9) All statements made herein, of my own knowledge, are true, and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made may be punishable by fine or imprisonment or both, under Section 1001 Title 18 of the U.S. code and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Dated: Feb. 13, 2004

Hong Xu

Hong Xu

Shb Instruments Model 109A

Instrument #71
7/13/2003 12:25:22 AMLoop 1
10 Hz nWbLoop 2
10 Hz nWb

Measurements

06-13-2003 00:25:03

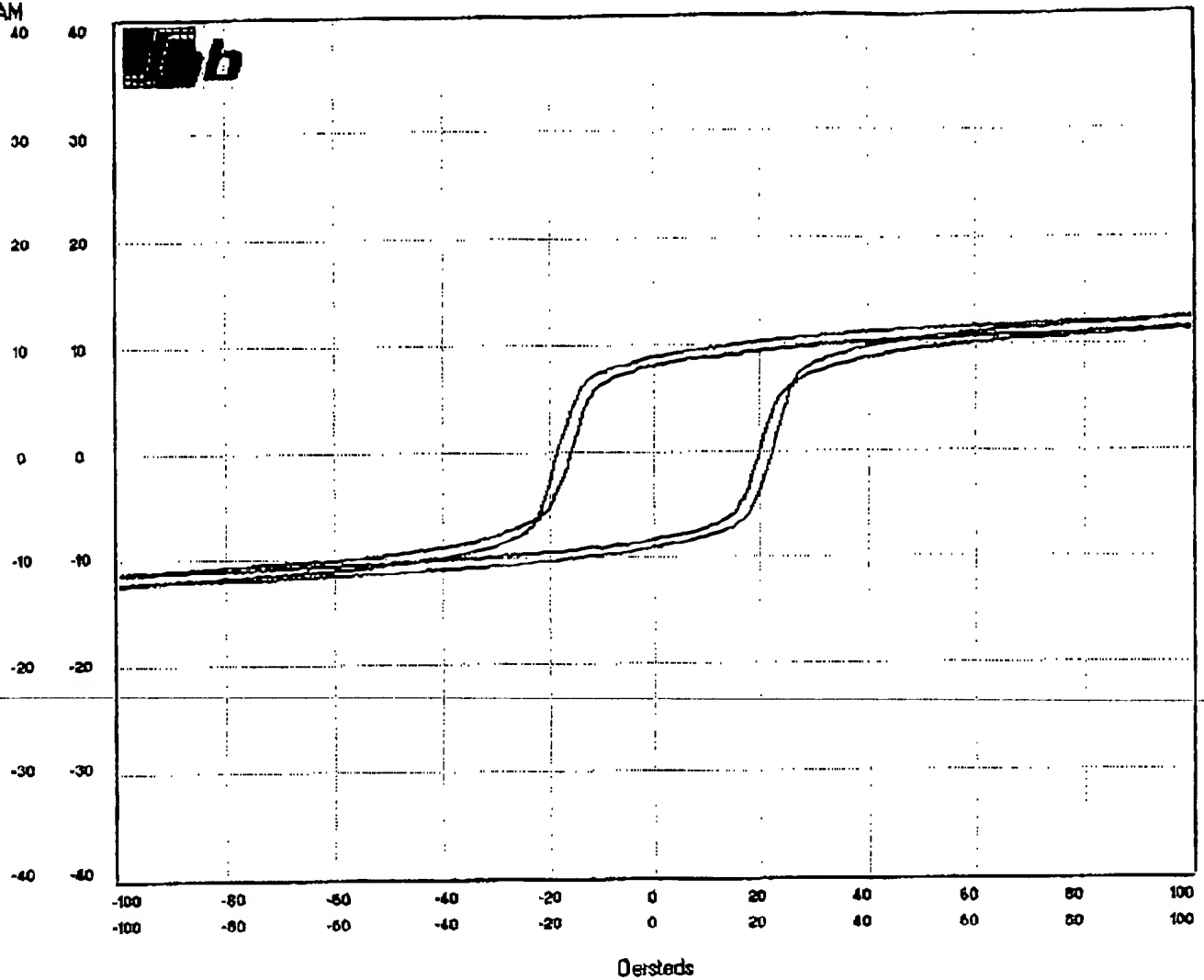
Procedure:

TEST	MEASUREMENT	CONSTANT	DRIVE	AVERAGES	FREQ	SIGMA
Hc	24.33 Oe		99.97 Oe	10	10 Hz	.0153 Oe

Sch stationary
#1

(Kakuno's paper)

Shb Instruments Model 109A

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10 Hz nWbLoop 2
10 Hz nWb

Measurements

06-13-2003 00:26:28

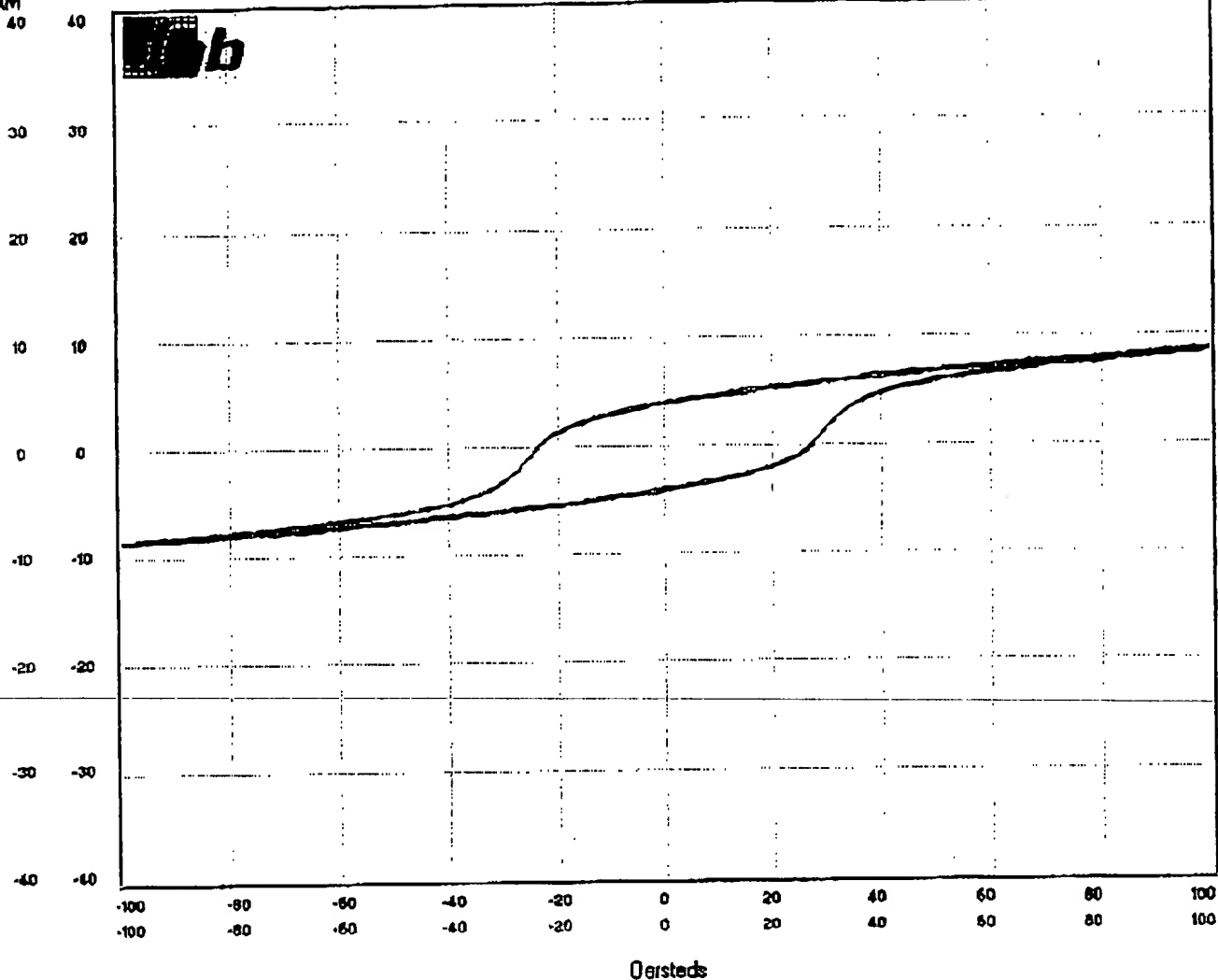
Procedure:

TEST	MEASUREMENT	CONSTANT	DRIVE	AVERAGES	FREQ	SIGMA
Hc	17.92 0e		99.97 0e	10	10 Hz	.0000 0e

SCH Stationary
#2

Chakuno's paper

Shb Instruments Model 109A

Instrument #71
7/13/2003 12:29:07 AMLoop 1
10 Hz nWbLoop 2
10 Hz nWb

Measurements

06-13-2003 00:28:44

Procedure:

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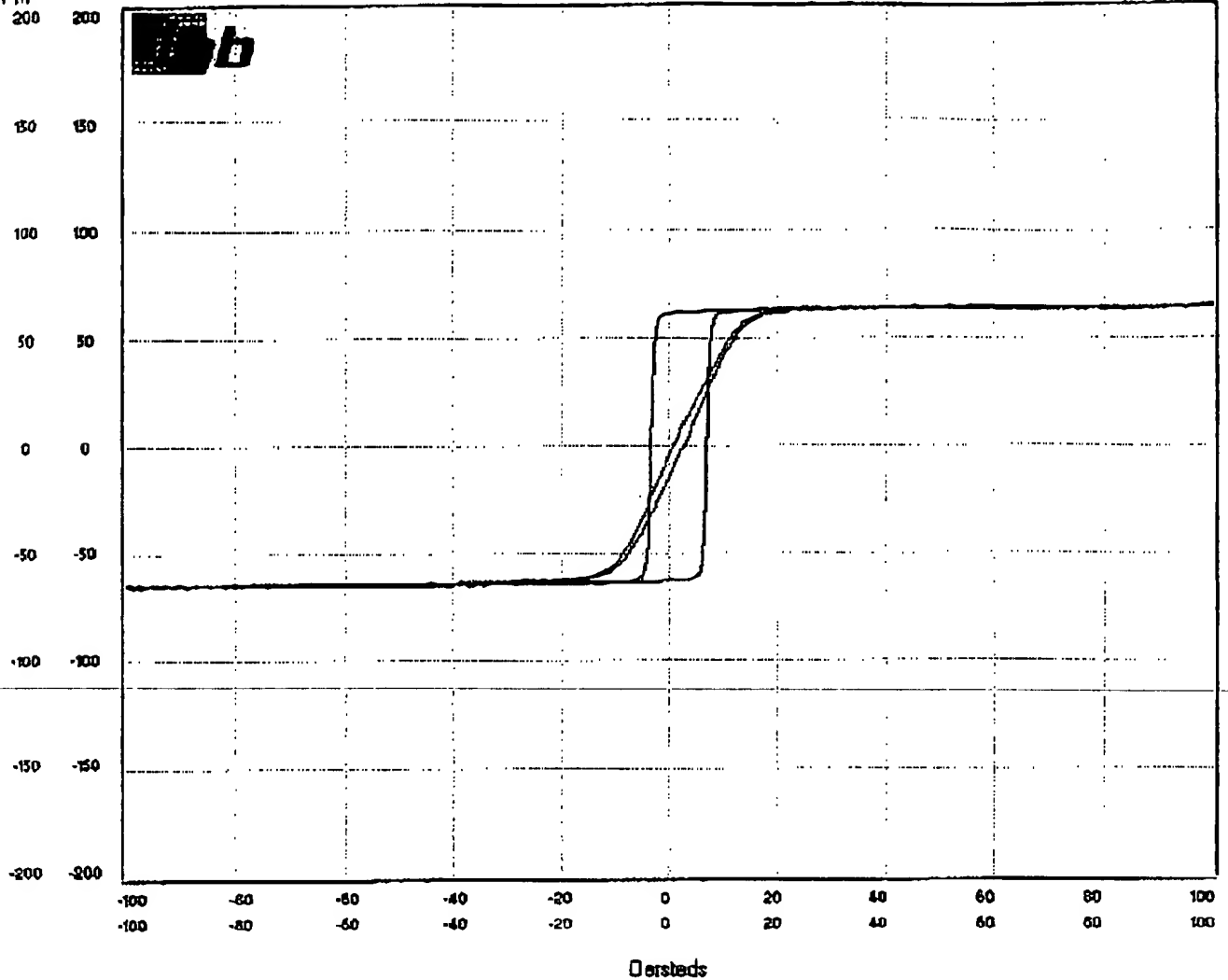
SCH stationary #3

(kakuno's paper)

Shb Instruments Model 109A

Instrument #71

7/11/2003 11:38:02 PM

Loop 1
10 Hz nWbLoop 2
10 Hz nWb

Measurements

06-11-2003 23:37:45

Procedure:

TEST	MEASUREMENT	CONSTANT	DRIVE	AVERAGES	FREQ	SIGMA
Bs	64.44 nWb		99.87 Oe	18	10 Hz	.2010 nWb

#22) (IBM patent application films)

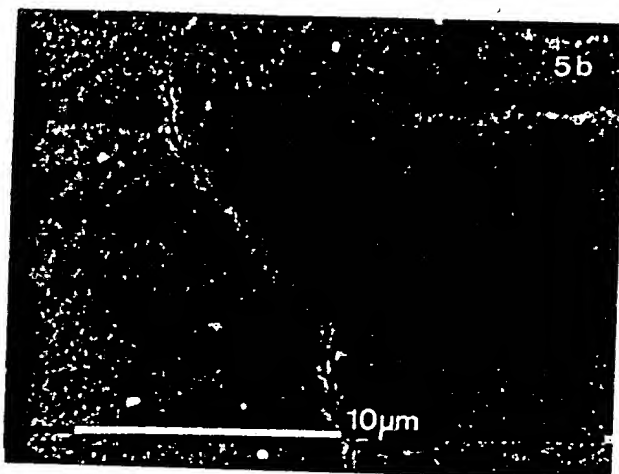
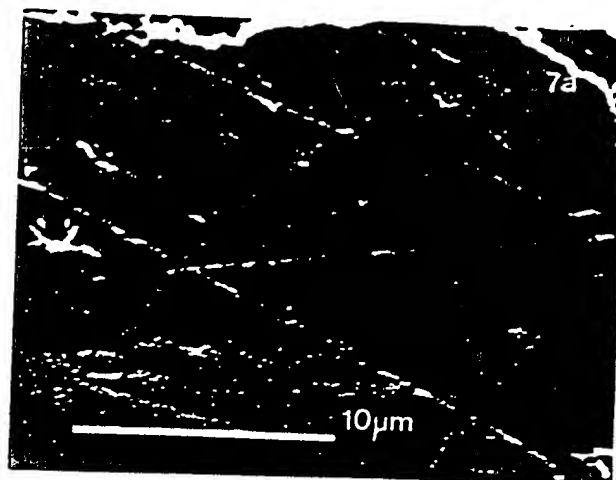
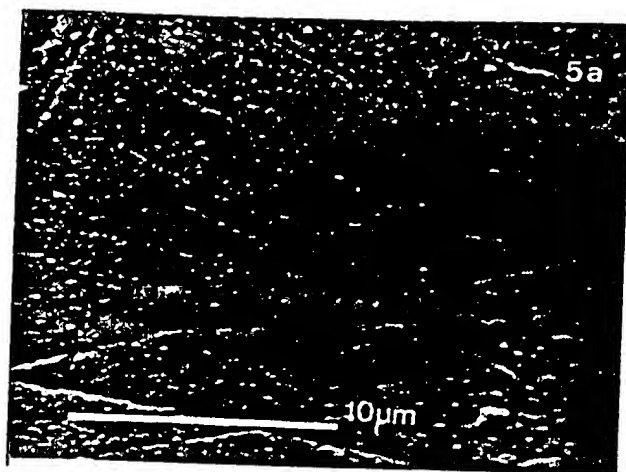


Fig. 5. SEM micrographs of Co_{0.7}Fe_{0.3} alloys showing the morphology as a function of cathodic potential during deposition: (a) cathodic potential of -1.0 V and (b) cathodic potential of -1.4 V.

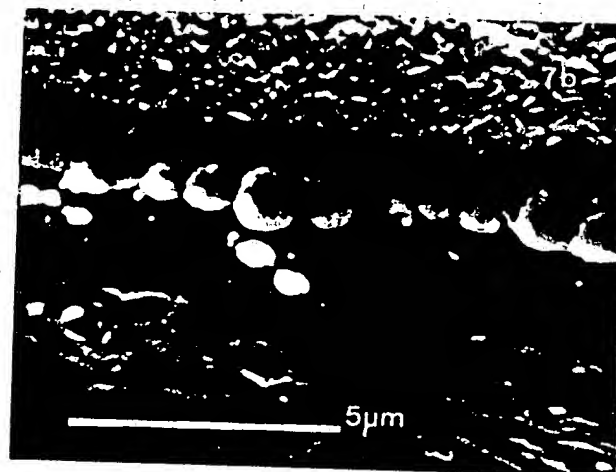


Fig. 7 Morphology of Co_{0.9}Fe_{0.1} alloys: (a) at the center of the deposit and (b) at the edge of the electrode.

rates the conclusion about an increase of stress in the Co-rich deposits.

Finally, Fig. 7 shows the morphology of Co_{0.9}Fe_{0.1} alloys in the center and in the edge of the deposits. At the edge of the electrode, a higher current density and a higher hydrogen evolution rate are expected due to the effect of concentration of the field. As a consequence, we can expect a

local enhancement of the pH value at edges which can originate a burning of the deposit by simultaneous precipitation of Fe(OH)₂ and Co(OH)₂ on the electrode.^{5,6,8} The bubble-shape morphology of the edges of the Cu electrodes with higher Co concentration seems to indicate the occurrence of the burning of the deposits shown in Fig. 7b. This effect on the alloy morphology is much less evident toward the center of the electrode. A fibrous-shaped structure at the edge can also be observed in the figure.

Conclusions

The mass-transfer mechanism occurring in the Co and Fe codeposition seems to be complex and probably involves intermediate compounds, such as Fe(OH)⁺ and Co(OH)⁺, to make possible the electrodeposition of alloys with the same Co/Fe ratio present in the bulk solution. However, despite complexity of electrodeposition mechanism Co_{0.7}Fe_{0.3} alloys with desired *x* values and good compositional uniformity can be easily obtained by potentiostatic deposition from simple sulfated baths.

The crystalline structure of the alloys creates texture over the whole range of alloy compositions. For high Fe concentration the deposits have a structure mostly bcc, whereas for high Co concentration the deposits are mostly hcp. A small fraction of fcc phase observed in deposits with low Fe concentrations indicates a disordered transition process as the structure is going from bcc to hcp structure. This transition occurs around *x* = 0.7 where some Co segregation occurs and heterogeneous morphology of deposits is observed.

In general, the morphology of alloys do not change drastically either as a function of the alloy concentration

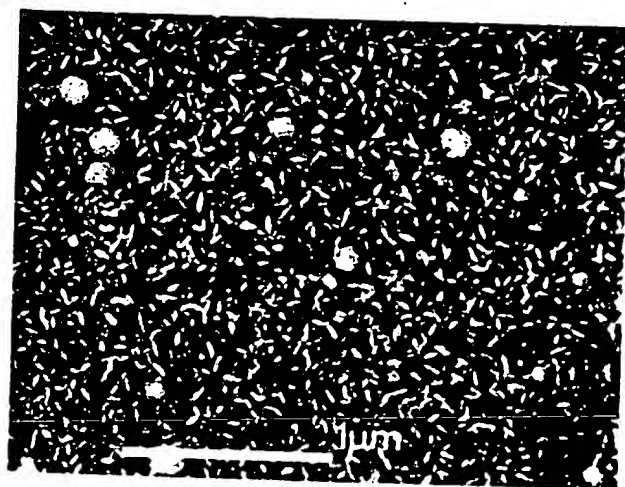
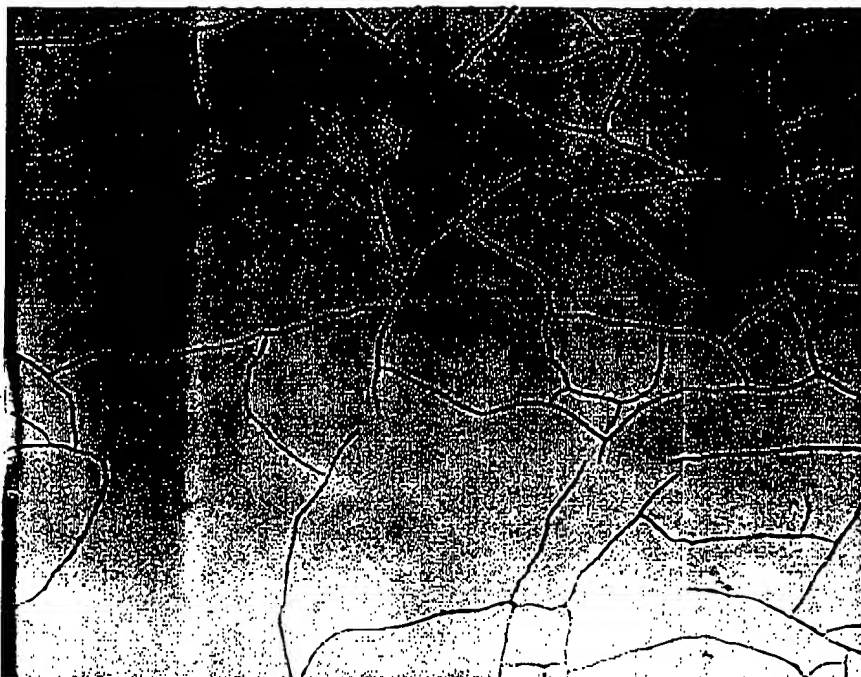
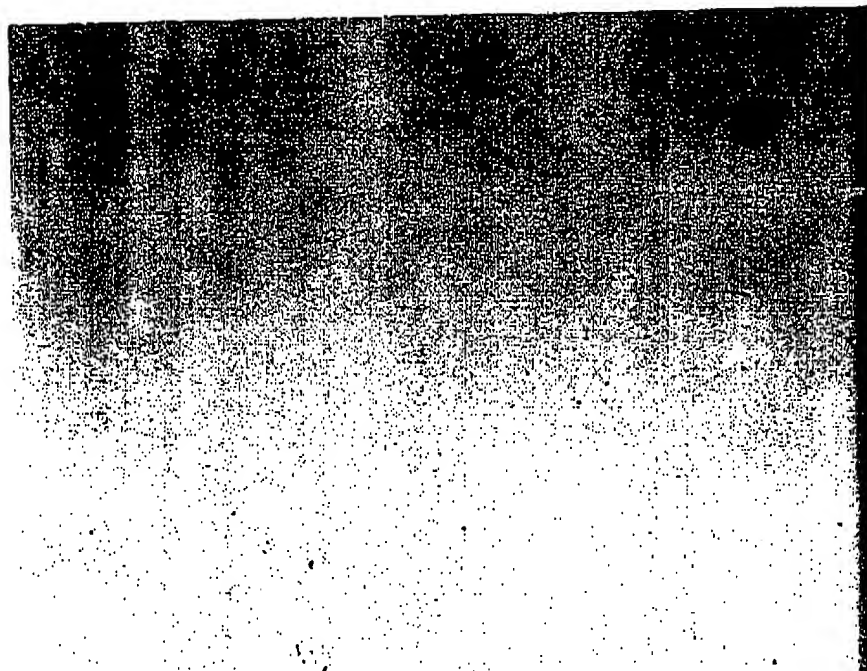


Fig. 6. SEM micrograph of the Co_{0.7}Fe_{0.3} alloys showing details of the morphology. Microcrack probably originates from strain relaxation during deposition is also shown.



Kakuno #217 paddel cell X25 Fe=69.0wt% thk=1.5um(T-2-03)



IBM Paddel cell X25 #221 Fe wt%=73.123 thk=7.537um T-2-03
CoFe

Exhibit 4

X-ray diffraction data for plated Kakuno film at Fe 43, 64 and 76 wt.% and inventive film at Fe 76wt.%:

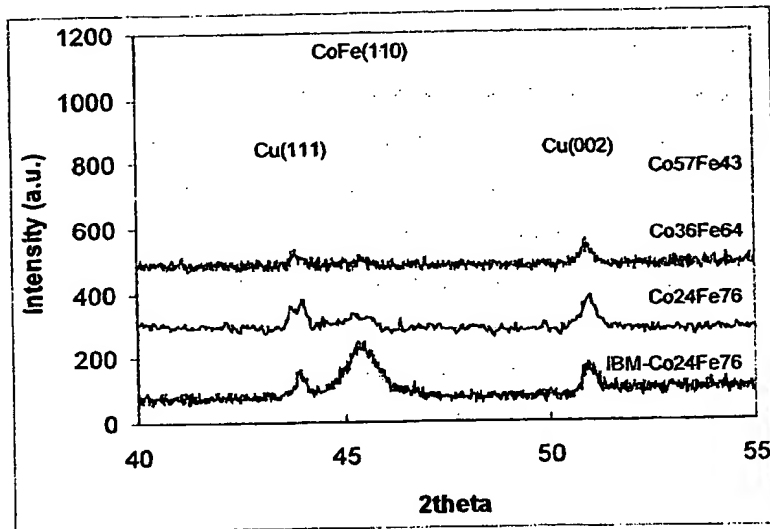


Figure 4 from Kakuno's paper

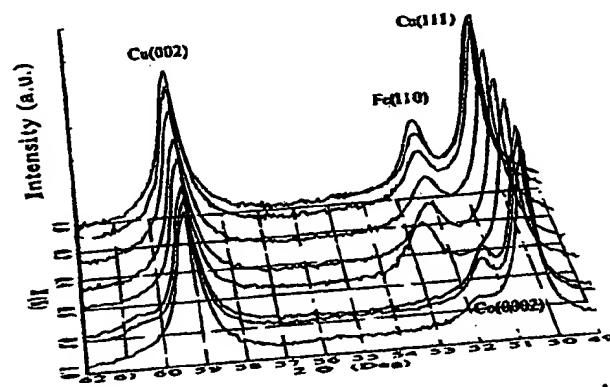


Fig. 4. X-ray diffraction patterns in Bragg-Brentano geometry, using Co K_α radiation, of CoFe_{1-x} alloys electrodeposited on Cu electrodes at cathodic potential of -1.2 V (V vs. Ag/AgCl). To facilitate comparison between diffractograms, a square root of the intensities in arbitrary units is shown.